DECLARATION

I, Satoshi NAKAMURA of 5-8, Eharacho 2-chome, Nakano-Ku, Tokyo, do hereby declare that I am well acquainted with the Japanese and English languages and that the attached English translation is a true translation from Japanese into English of Japanese Patent Application No. Hei 10-217433 filed with the Japanese Patent Office on July 31, 1998.

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PHOTOMASK BLANK, PHOTOMASK, AND METHODS OF MANUFACTURING THE SAME

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PHOTOMASK BLANK, PHOTOMASK, AND METHODS OF MANUFACTURING THE SAME

[CLAIMS]

[Claim 1]

A photomask blank used to manufacture a photomask used as an exposure original in a photolithography process, comprising: a thin film including chromium carbide with a crystal grain diameter of 3 to 7 nm.

[Claim 2]

The photomask blank according to claim 1, wherein said thin film is formed in an atmosphere of a mixed gas including helium.

[Claim 3]

The photomask blank according to claim 1 or claim 2, wherein said thin film is provided over a shading film provided over a transparent substrate.

[Claim 4]

The photomask blank according to any one of claims 1 to 3, wherein film thickness of said thin film is 250 to 1400 angstroms.

[Claim 5]

A photomask, wherein patterning is performed by applying etching to the photomask blank according to any one of claims 1 to 4.

[Claim 6]

A method of manufacturing a photomask blank in which a spattering target is disposed in a vacuum chamber, and a thin film is formed over a transparent substrate by reactive sputtering,

wherein said thin film is formed in an atmosphere of a mixed gas including helium.

[Claim 7]

A method of manufacturing a photomask blank in which a spattering

target is disposed in a vacuum chamber, and a thin film is formed over a transparent substrate by reactive sputtering,

wherein formation is made at a deposit rate of 6 nm/sec or lower in an atmosphere of a mixed gas.

[Claim 8]

The method of manufacturing a photomask blank according to claim 6 or 7, wherein the deposit rate of said thin film is 2 nm/sec to 6 nm/sec.

[Claim 9]

The method of manufacturing a photomask blank according to any one of claims 6 to 8, wherein the thin film is formed by controlling a flow rate of the helium gas contained in the mixed gas such that a crystal grain diameter of said thin film becomes 3 to 7 nm.

[Claim 10]

The method of manufacturing a photomask blank according to any one of claims 6 to 9, wherein a helium gas content in said mixed gas is 30 vol% or more.

[Claim 11]

The method of manufacturing a photomask blank according to claim 10, wherein the helium gas content in said mixed gas is 30 to 90 vol%.

[Claim 12]

The method of manufacturing a photomask blank according to claim 11, wherein the helium gas content in said mixed gas is 40 to 65 vol%.

[Claim 13]

The method of manufacturing a photomask blank according to any one of claims 6 to 12, wherein said thin film is mainly composed of chromium.

[Claim 14]

The method of manufacturing a photomask blank according to any one of claims 6 to 13, wherein said thin film is a thin film including a film of chromium carbide.

[Claim 15]

The method of manufacturing a photomask blank according to any one of claims 7 to 13, wherein said thin film is a thin film including an anti-reflective film.

[Claim 16]

A method of manufacturing a photomask, wherein a mask pattern is formed by using the photomask blank according to any one of claims 7 to 15 as a material and selectively removing said thin film in said photomask blank.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of Industrial Application]

The present invention relates to a photomask blank used to manufacture a photomask used as an original for photolithography method for fine processing in the process of manufacturing a semiconductor integrated circuit device or the like, to a photomask that is manufactured from this photomask blank, and to methods of manufacturing the same.

[0002]

[Prior Art]

Photography technique has come to be used in recent years in the process of forming wiring and other regions in the manufacture of semiconductor integrated circuit devices. Known photomask blanks used as the exposure original in the photography process include those with a basic structure in which a shading film of chromium (Cr) is formed over a transparent substrate, and those with a multilayer structure in which an anti-reflective film such as a chromium oxynitride (CrON) film is further laminated in order to prevent reflection on the shading film surface produced by the exposure light.

[0003]

The method employed to manufacture a photomask blank such as this

involves introducing a transparent substrate into a vacuum chamber in which a sputtering target has been disposed, and forming a shading film over the transparent substrate by reactive sputtering. With this film formation method, it is possible to raise the sputtering power in order to enhance the photomask blank productivity. Unfortunately, while raising the sputtering power does raise the film formation rate (that is, the deposition rate), if any impurities are present in the target, there is the possibility that there will be a higher incidence of particle generation in the formed thin film, which lowers the yield.

[0004]

[Problems to Be Resolved by the Invention]

In view of this, in an effort to enhance productivity through a higher yield, the inventors investigated lowering the sputtering power in order to lower the film formation rate (that is, the deposition rate). It was found, however, that merely focusing on lowering the power as one of the sputtering conditions only results in the following new problems.

[0005]

Specifically, it was learned that if the film formation rates of the thin films that make up the photomask blank are each lowered, in general, the crystal grains of the film deposited on the transparent substrate will be larger, and this will be attended by the generation of extremely large film stress caused by the crystal grains pulling on one another. The mechanism by which this film stress is generated is not entirely clear, but it is thought to be attributable to the deposition rate of the films. Particularly, in the case of a photomask blank made up of chromium-based thin films, such as a photomask blank having a three-layer structure of CrN/CrC/CrON, it was found that this problem is serious with the CrC thin film, which is the thickest of the three.

[0006]

Tensile stress occurs and leads to substrate warping in a photomask blank including thin films manufactured through a series of manufacturing steps and having the above-mentioned film stress, and in the photomask obtained by patterning this photomask blank. Therefore, if a photomask is produced from a photomask blank such as this, there is the danger that the patterning precision will not be as designed, producing defective products. Specifically, wiring design is important in the manufacture of a semiconductor integrated circuit device, and if a photomask such as this is used to transfer a pattern to a semiconductor wafer or the like, the pattern will not be formed as designed on the semiconductor wafer, resulting in circuit malfunction, and therefore this photomask cannot be used and is a defective product.

[0007]

In view of this, the inventors investigated a method of manufacturing a photomask blank with which it is possible to avoid the problem of film stress in thin films formed under film formation conditions involving sputtering at low power as mentioned above.

[0008]

Aside from the sputtering power conditions, the material of the thin films that make up the photomask blank is determined on the basis of the following sputtering conditions, and the inventors therefore conducted investigations and experiments into various parameters.

[0009]

First, they investigated the gas pressure used in sputtering. Gas pressure was the only sputtering condition they focused on, and other parameters were kept constant in the experiments and investigations.

[0010]

Figure 7 is a graph of the relationship between the gas pressure and the change in substrate warping attributable to film stress. It is clear from this

graph that there is less change when the gas pressure is lower, and more change when the gas pressure is higher. In other words, these investigative results reveal that it is undesirable for the gas pressure to be raised because the deposition rate will be too low, and that it is undesirable for the gas pressure to be lowered because reduction in film quality by stress is unavoidable though film thickness is not especially changed.

[0011]

Next, the types of gas that make up the mixed gas were investigated. Experiments and investigations were conducted for when the gas components were the only sputtering condition examined, the power and gas pressure were not varied, and other parameters were set to constant values.

[0012]

As for the mixed gas used in sputtering, a reactive gas and an inert gas are mixed and used. The inventors first turned their attention to the reactive gas, and conducted sputtering adopting nitrogen (N) atoms, for example, and as a result, it was found that particles are generated by abnormal discharge. It was thus revealed that there is a limit to how many reactive gas N (nitrogen) atoms can be introduced, so the components of the mixed gas must be used in appropriate amounts. For instance, in view of an N gas controlling film quality, the amount of nitrogen monoxide (NO) gas introduced was reduced in order to make the film thickness of the CrON film as an anti-reflective film thinner, but this generated film stress due to a decrease in nitrogen (N) atoms in the CrON film. On the other hand, excessively increasing the amount of nitrogen monoxide (NO) gas introduced during the formation of the above-mentioned CrON film resulted in abnormal discharge during sputtering due to the effect of the nitrogen (N) atoms, and consequently there arose the problem that the above-mentioned problem with particles resulted in poor film quality . Therefore, it was revealed that even if the amount of nitrogen (N) atoms introduced as the reactive gas is optimized, it will still be very difficult to

achieve optimal sputtering conditions in terms of the relation between introduction amount and film quality.

[0013]

Thus, when films were formed by changing the various parameters of the film formation conditions (film sputtering conditions) for film stress, namely, the gas pressure, gas flow ratio, sputtering power, and so forth, it was extremely difficult to control both the optical characteristics and the film quality (changes in the optical characteristics of the formed film, changes in film quality, etc.). Therefore, an attempt was made to achieve the above-mentioned goal by looking for an inert gas with good controllability as the type of gas that makes up the above-mentioned mixed gas under the condition that the power during sputtering will be lowered.

[0014]

The present invention was conceived in light of the above problems, and it is an object thereof to provide a photomask blank and photomask that have thin films with low film stress, good film quality, and can be mass-produced at a high yield, which is accomplished by changing the constitution of the mixed gas, and to provide methods of manufacturing the same.

[0015]

[Means for Resolving the Problems]

The photomask blank of the invention of claim 1, used to manufacture a photomask used as an exposure original in a photolithography process, comprising: a thin film including chromium carbide with a crystal grain diameter of 3 to 7 nm.

[0016]

The photomask blank of the invention of claim 2, in claim 1, wherein said thin film is formed in an atmosphere of a mixed gas including helium.

[0017]

The photomask blank of the invention of claim 3, in claim 1 or claim 2,

wherein said thin film is provided over a shading film provided over a transparent substrate.

[0018]

The photomask blank of the invention of claim 4, in any one of claims 1 to 3, wherein film thickness of said thin film is 250 to 1400 angstroms.

[0019]

The photomask of the invention of claim 5, wherein patterning is performed by applying etching to the photomask blank according to any one of claims 1 to 4.

[0020]

The method of manufacturing a photomask blank of the invention of claim 6 in which a spattering target is disposed in a vacuum chamber, and a thin film is formed over a transparent substrate by reactive sputtering; wherein said thin film is formed in an atmosphere of a mixed gas including helium.

[0021]

The method of manufacturing a photomask blank of the invention of claim 7 in which a spattering target is disposed in a vacuum chamber, and a thin film is formed over a transparent substrate by reactive sputtering; wherein formation is made at a deposit rate of 6 nm/sec or lower in an atmosphere of a mixed gas.

[0022]

The method of manufacturing a photomask blank of the invention of claim 8, in claim 6 or 7, wherein the deposit rate of said thin film is 2 nm/sec to 6 nm/sec.

[0023]

The method of manufacturing a photomask blank of the invention of claim 9, in any one of claims 6 to 8, wherein the thin film is formed by controlling a flow rate of the helium gas contained in the mixed gas such that

a crystal grain diameter of said thin film becomes 3 to 7 nm.

[0024]

The method of manufacturing a photomask blank of the invention of claim 10, in any one of claims 6 to 9, wherein a helium gas content in said mixed gas is 30 vol% or more.

[0025]

The method of manufacturing a photomask blank of the invention of claim 11, in claim 10, wherein the helium gas content in said mixed gas is 30 to 90 vol%.

[0026]

The method of manufacturing a photomask blank of the invention of claim 12, in claim 11, wherein the helium gas content in said mixed gas is 40 to 65 vol%.

[0027]

The method of manufacturing a photomask blank of the invention of claim 13, in any one of claims 6 to 12, wherein said thin film is mainly composed of chromium.

[0028]

The method of manufacturing a photomask blank of the invention of claim 14, in any one of claims 6 to 13, wherein said thin film is a thin film including a film of chromium carbide.

[0029]

The method of manufacturing a photomask blank of the invention of claim 15, in any one of claims 7 to 13, wherein said thin film is a thin film including an anti-reflective film.

[0030]

The method of manufacturing a photomask of the invention of claim 16, wherein a mask pattern is formed by using the photomask blank according to any one of claims 7 to 15 as a material and selectively removing said thin

film in said photomask blank.

[0031]

[Mode for Carrying out the Invention]

(Example 1)

Figure 1 is a schematic cross section of the photomask blank pertaining to Example 1, and Figure 2 is a schematic cross section of the photomask pertaining to Example 1.

[0032]

With the photomask blank 1 pertaining to Example shown in Figure 1, a quartz glass substrate measuring 5 inches × 5 inches × 0.09 inch and whose main surface and end faces had undergone precision polishing was used as the transparent substrate 2. Over this transparent substrate 2 were formed a chromium nitride (CrN) film (N: 20 at%; film thickness: 150 angstroms) as a first shading film 3, a chromium carbide (CrC) film (C: 6 at%; film thickness: 600 angstroms) as a second shading film 4, and a chromium oxynitride (CrON) film (film thickness: 250 angstroms) as an anti-reflective film 5.

[0033]

Here, as described above, for example, CrON film is used as an anti-reflective film 5. The surface reflectance of the anti-reflective film 5 is determined by the amounts of oxygen and nitrogen contained in the anti-reflective film 5, and is controlled by suitably checking the film thickness. To control surface reflectance, the composition is generally selected so as to minimize reflectance dependence with respect to film thickness near the wavelength of the exposure light.

[0034]

The photomask 11 shown in Figure 2 is formed by etching the photomask blank 1 of Figure 1.

[0035]

Next, the characteristics of the photomask blank 1 in terms of

manufacturing, and the effect thereof as a photomask blank, will be described.

Figures 3 and 4 are schematic cross sections illustrating the methods for manufacturing the photomask blank, and the photomask of Example 1 of the present invention, respectively.

[0036]

Here, a CrN film with a thickness of 150 angstroms was formed as the first shading film 3 as shown in Figure 3 (a) by reactive sputtering using the transparent substrate 2 measuring 5 inches × 5 inches × 0.09 inch which was obtained by undergoing a precision polishing to main surface and side faces of the quartz substrate, and using a chromium target in a mixed gas atmosphere of argon and nitrogen (Ar: 80 vol%, N_2: 20 vol%, pressure: 0.3 Pa). The CrN film thus obtained had a nitrogen content of 20 at%.

[0037]

In addition to quartz, the above-mentioned transparent substrate 1 can also be fluorite, various types of glass (such as soda lime glass, aluminosilicate glass, or aluminoborosilicate glass), or the like.

[0038]

Then, a CrC film with a thickness of 600 angstroms was formed as the second shading film 4 as shown in Figure 3 (b) by reactive sputtering using a chromium target in a mixed gas atmosphere composed of argon, methane, and helium (Ar: 30 vol%, CH_4: 10 vol%, He: 60 vol%, pressure 0.3 Pa). The carbon content in the CrC film of the above photomask blank was measured and found to be 6 at%, and the etching rate was 0.3 nm/sec.

[0039]

The method of the present invention for manufacturing a photomask blank solves the problems mentioned above by having the helium serving as the inert gas be contained as a type of mixed gas. Figure 3 (b) here shows an example in which the helium content in the mixed gas is 60 vol%, but the proportions in which the gases are mixed in this mixed will be discussed in

detail below on the basis of experimental results.

[0040]

A CrON film with a thickness of 250 angstroms was formed as the anti-reflective film 5 as shown in Figure 3 (c) over the above-mentioned CrC film by reactive sputtering using a chromium target in a mixed gas atmosphere of argon and nitrogen monoxide (Ar: 80 vol%, NO: 20 vol%, pressure: 0.3 Pa), with this film being formed continuously with the CrC film. Ultrasonic washing was performed to obtain the photomask blank 1.

[0041]

As shown in Figure 4 (a), a resist 6 was applied by coating over the CrON film serving as the anti-reflective film 5, and this was subjected to pattern exposure and developing to form a resist pattern as shown in Figure 4 (b). CrON not only has an anti-reflective function, but also has an anti-oxidizing function, and consequently its durability is good and it exhibits good characteristics for a photomask blank. Thus, adhesion is good with the resist used in a subsequent step, and the above-mentioned patterning can be carried out stably and to high precision. Here, the sheet resistance value of the finally obtained CrN/CrC/CrON film was measured, whereupon conductivity was good, being 25 ohms per square or less. This indicates that charge tend not to build up between the CrON film and the resist during electron exposure.

[0042]

Then, after the above-mentioned patterning, an etching solution produced by adding pure water to 165 g of ceric ammonium nitrate and 42 mL of perchloric acid (70% concentration) to bring the total to 1000 mL was held at 19 to 20 centigrade, wet etching was performed with this etching solution, and the CrON film was patterned as shown in Figure 4 (c) using the above-mentioned resist pattern as a mask.

[0043]

The patterning of the CrON film, the patterning of the CrC film, and the patterning of the CrN film were continuously carried out through this wet etching, and after the above-mentioned resist was removed by a standard method using an oxygen plasma or sulfuric acid, the photomask 11 having the desired pattern was obtained as shown in Figure 4 (d).

[0044]

The helium (He) content in the mixed gas used in the present invention will now be described. First, because nitrogen is admixed as a film formation component during the formation of the CrN film, the film is thin, so a good thin film can be obtained as above by controlling the nitrogen used as the reactive gas in the mixed gas. As to the CrC film, the mixed gas contained not only argon, but also 60 vol% helium, is used as the reactive gas in the mixed gas.

[0045]

Figure 5 is a graph of the relationship between the helium content in the mixed gas, and the change in substrate warping attributable to stress. If the helium content is increased in order to ensure good control of sputtering, then the discharge will be unstable, and the change will increase too much, so the helium content in the mixed gas must be no more than 90 vol%. Due to the relationship with film thickness and gas pressure, the highest film quality was achieved when the content in the mixed gas was about 60 to 65 vol%. The deposition rate of the thin film at this time was approximately 4 nm/sec, and the film stress was nothing.

[0046]

Even when the helium content in the mixed gas was about 40 vol%, a good film could be obtained by adjusting the sputtering power. When the helium content in the mixed gas was lowered to about 30 vol%, the film stress was measured, and the substrate warping was within a range that can be identified as passable as a photomask blank and a photomask produced by

using this.

[0047]

When the etching rate is considered, it is preferable for the content of components other than helium in the mixed gas to be adjusted according to the film quality.

[0048]

Although not shown in the graph, a photomask blank was produced by further lowering the sputtering power and setting the thin film deposition rate to approximately 2 nm/sec, but no film stress that would pose a problem was generated, and the photomask blank, as well as the photomask produced using this blank, were within the passable range. Conversely, when a photomask blank was produced by raising the sputtering power and setting the thin film deposition rate to approximately 6 nm/sec, no particles that would pose any particular problem were observed in the thin film, and the photomask blank, as well as the photomask produced using this blank, were within the passable range.

[0049]

According to methods of manufacturing a photomask blank and a photomask shown in Example 1, by using helium as the mixed gas in sputtering on forming a chromium carbide layer, diameters of grains forming the CrC film and the CrON film reduce to be 3 to 7 nm, and a favorable thin film without film stress is obtained. This mechanism remains uncertain, but the CrC crystal does not become amorphous though it is fine-grained, and it is considered that as a result of entering helium (He) atoms less related by incorporation of Cr grains, the CrC film and CrON film are formed while the growth of the film of the Cr crystal is being prevented.

[0050]

Next, the film stress which was conventionally the problem was investigated concerning the obtained photomask blanks. A commercially

available apparatus was used to measure the film stress of the photomask blanks produced in this manner, whereupon the optical density was 3.0 and the surface reflectance was 12% at a wavelength of 365 nm. Also, in all the films, there were no film defects, meaning that film quality was good.

[0051]

Thus, at least when forming the CrC film and CrON film, film stress can be suppressed by introducing helium gas into the atmosphere gas, and a photomask blank with good film quality can be obtained while ensuring a high yield, without any adverse effect of impurities from the target. Also, no particular film stress occurred when the CrC film was formed in a thickness of approximately 250 to 1100 angstroms and the CrON film in a thickness of approximately 200 to 300 angstroms, and it was possible to obtain a good photomask blank, as well as a good photomask using this blank. It is also possible to form CrN, CrC and CrON continuously in a state in which He remains in the vacuum chamber during formation of the CrC film and CrON film. A photomask blank having even better film quality is obtained in this case.

[0052]

(Example 2)

There are no particular restrictions on the sputtering apparatus in Example 1, but we described an example of forming a film by reactive sputtering which is applicable to a standard sputtering apparatus. In other words, Example 1 can be applied to a method in which, for example, a sputtering target is disposed within a vacuum chamber, and the various types of film are formed one at a time in each reaction chamber by batch process and reactive sputtering.

[0053]

The use of an inline continuous sputtering apparatus in the manufacture of photomask blanks has become prevalent in recent years in

order to boost productivity. In view of this, it is conceivable that an inline continuous sputtering apparatus will be used in the method of the present invention for manufacturing a photomask blank in an effort to achieve further increases in productivity while achieving a high yield. In Example 2, we will describe a case in which an inline continuous sputtering apparatus is applied.

[0054]

The method described in Example 2 is a manufacturing method in which the technique of Example 1 is applied to inline continuous sputtering, which is an effective method for forming films that lends itself to mass production. Specifically, the difference between an ordinary sputtering apparatus and the inline continuous sputtering apparatus of Example 2 is that a plurality of targets are disposed in an inert gas atmosphere such as argon, and a plurality of types of film are continuously formed on transparent substrates while the transparent substrates are continuously conveyed between sputtering targets at a specific conveyance speed.

[0055]

Figure 6 shows a simplified diagram of an inline continuous sputtering apparatus. The inline continuous sputtering apparatus continuously applies films over several transparent substrates carried on a pallet, and a series of film applications is carried out while the substrates are conveyed through a single vacuum chamber. Therefore, since power in sputtering is applied similarly to all the thin films in this case, the setting of each parameter is important in order to obtain good quality in all the films.

[0056]

In this case, the substrate conveyance speed is closely linked to production efficiency in inline continuous sputtering. Namely, in such a spattering apparatus, when sputtering is performed at a lower substrate conveyance speed, the deposition rate is also decreased. Consequently, as well as Example 1, though not only does production efficiency drop, but film

stress also occurs, when compared with the Example, particles will not tend to be produced in the pallets for holding the substrates and the conveyance mechanism that conveys the pallets.

[0057]

The transparent substrates 2 composed of quartz glass and measuring 5 inches × 5 inches × 0.09 inch and whose main surface and end faces have undergone precision polishing are put on a substrate holder (pallet) and introduced into the inline continuous sputtering apparatus shown in Figure 6. In the simplest terms, this inline sputtering apparatus consists of three chambers as shown in Figure 6: an entry chamber 21, a sputtering chamber (vacuum chamber) 22, and an exit chamber 23. These chambers are separated by partitions. The transparent substrates 2 loaded on the pallet are conveyed in the direction of the arrow in the figure. The structure of the various chambers will be described in the pallet conveyance direction.

[0058]

The entry chamber 21 is purged of air to create a vacuum on the inside. In the next chamber, the sputtering chamber 22, are formed shading films, such as chromium nitride (CrN)(the first shading film) and chromium carbide (CrC)(the second shading film), and the anti-reflective film, such as chromium oxynitride (CrON). In other words, the film formation steps illustrated in Figure 3 are carried out. Although not shown in the figures, a plurality of chromium targets for forming the first and second shading films and the anti-reflective film are provided inside the sputtering chamber 22, and a plurality of valves for introducing atmosphere gas are provided near these targets. The last chamber, the exit chamber 23, is purged of air to create a vacuum on the inside, just as with the entry chamber 21.

[0059]

When a photomask blank is manufactured using the inline continuous sputtering apparatus described above, the first step is to introduce a pallet

loaded with the quartz glass transparent substrates 2 into the entry chamber 21. The entry chamber 21 is then changed from atmospheric pressure to a vacuum, after which the pallet is conveyed into the sputtering chamber 22.

[0060]

In this sputtering chamber 22, the transparent substrates 2 loaded on the pallet are conveyed at a speed of 25 cm/min. At the first target, a mixed gas of Ar and N_2 (Ar: 80 vol%, N_2: 20 vol%) is introduced through the first valve, and a chromium nitride (CrN) film is formed as the first shading film 3 (see Figure 3 (a)) in a thickness of 150 angstroms by reactive sputtering. At the second target, a mixed gas of Ar, CH_4, and He (Ar: 30 vol%, CH_4: 10 vol%, He: 60 vol%) is introduced through the second valve, and a chromium carbide (CrC) film is formed as the second shading film 4 (see Figure 3 (b)) in a thickness of 600 angstroms by reactive sputtering. Then, at the third target, a mixed gas of Ar and NO (Ar: 80 vol%, NO: 20 vol%) is introduced through the third valve, and a chromium oxynitride (CrON) film is formed as the anti-reflective film 5 (see Figure 3 (c)) in a thickness of 250 angstroms by reactive sputtering. Three layers of film are thus formed continuously. The pressure inside the sputtering chamber 22 during the film formation was 0.3 Pa.

[0061]

After this, the pallet is moved into the vacuum-purged exit chamber 23. Once the sputtering chamber 22 and the exit chamber 23 have been completely separated by the partition, the exit chamber 23 is returned to atmospheric pressure. This yields a formed photomask blank. The pallets are continuously introduced, one after another, into the sputtering chamber 22 when the entry chamber 21 has reached the same state of vacuum as the sputtering chamber 22, so that at all times a plurality of pallets have been introduced into the sputtering chamber 22.

[0062]

A commercially available apparatus was used to measure the film

stress of the photomask blanks produced in this manner, whereupon the optical density was 3.0 and the surface reflectance was 12% at a wavelength of 365 nm. Also, no particles were generated from the pallets and there were no film defects, meaning that film quality was good.

[0063]

When the introduction of helium gas into the atmosphere gas in the formation of at least a chromium carbide film (CrC), allowed film stress to be suppressed and made it possible to obtain a film with no film stress even in the chromium oxynitride (CrON) film that was continuously formed. Furthermore, the application of inline continuous sputtering allowed a photomask blank with good film quality to be obtained while still permitting mass production.

[0064]

[Effect of the Invention]

The present invention, as described in detail above, makes it possible to obtain a photomask blank and photomask that have thin films with low film stress, good film quality, and can be mass-produced at a high yield.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1]

This is a schematic cross section of the photomask blank in Example of the present invention.

[FIG. 2]

This is a schematic cross section of the photomask in Example of the present invention.

[FIG. 3]

This is a diagram of the procedure in the steps (a) to (c) for manufacturing the photomask blank in Example of the present invention.

[FIG. 4]

This is a diagram of the procedure in the steps (a) to (c) for

manufacturing the photomask in Example of the present invention.

[FIG. 5]

This is a graph of the relationship between helium content and substrate warping (change in flatness) when the manufacturing method of the present invention is carried out.

[FIG. 6]

This is a simplified structural diagram of an inline continuous sputtering apparatus for implementing the manufacturing method of the present invention.

[FIG. 7]

This is a graph of the conventional relationship between gas pressure and substrate warping (change in flatness).

[Explanations of Letters of Numerals]

1 ... photomask blank;

2 ... transparent substrate;

3 ... first shading film (CrN film);

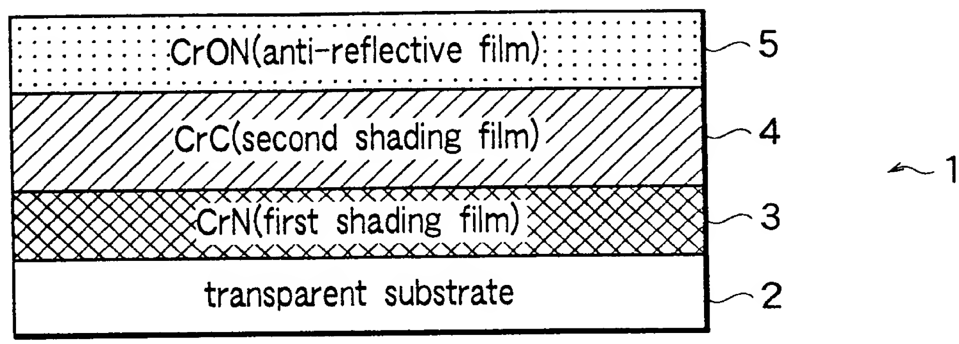
4 ... second shading film (CrC film);

5 ... anti-reflective film (CrON film);

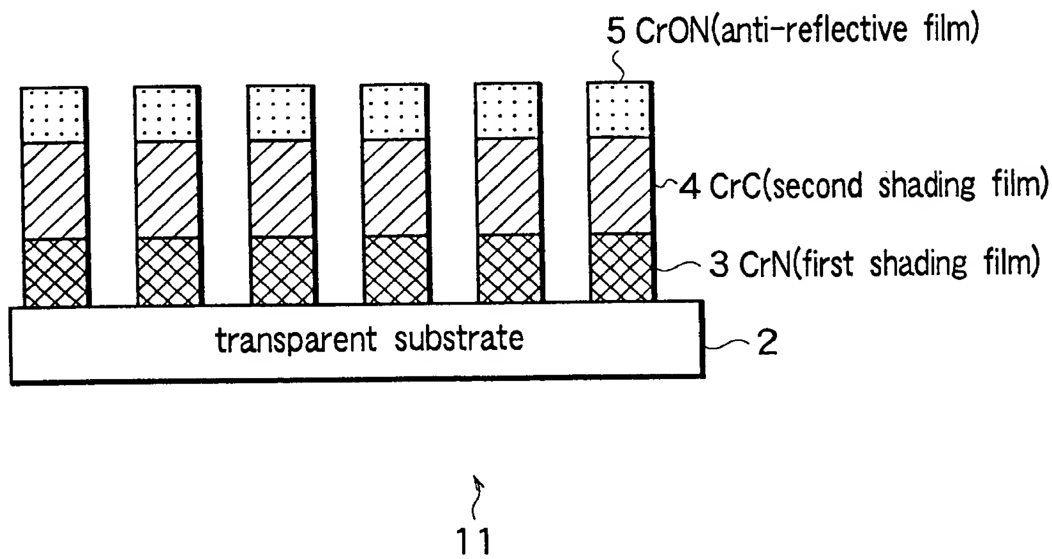
6 ... resist;

11 ... photomask.

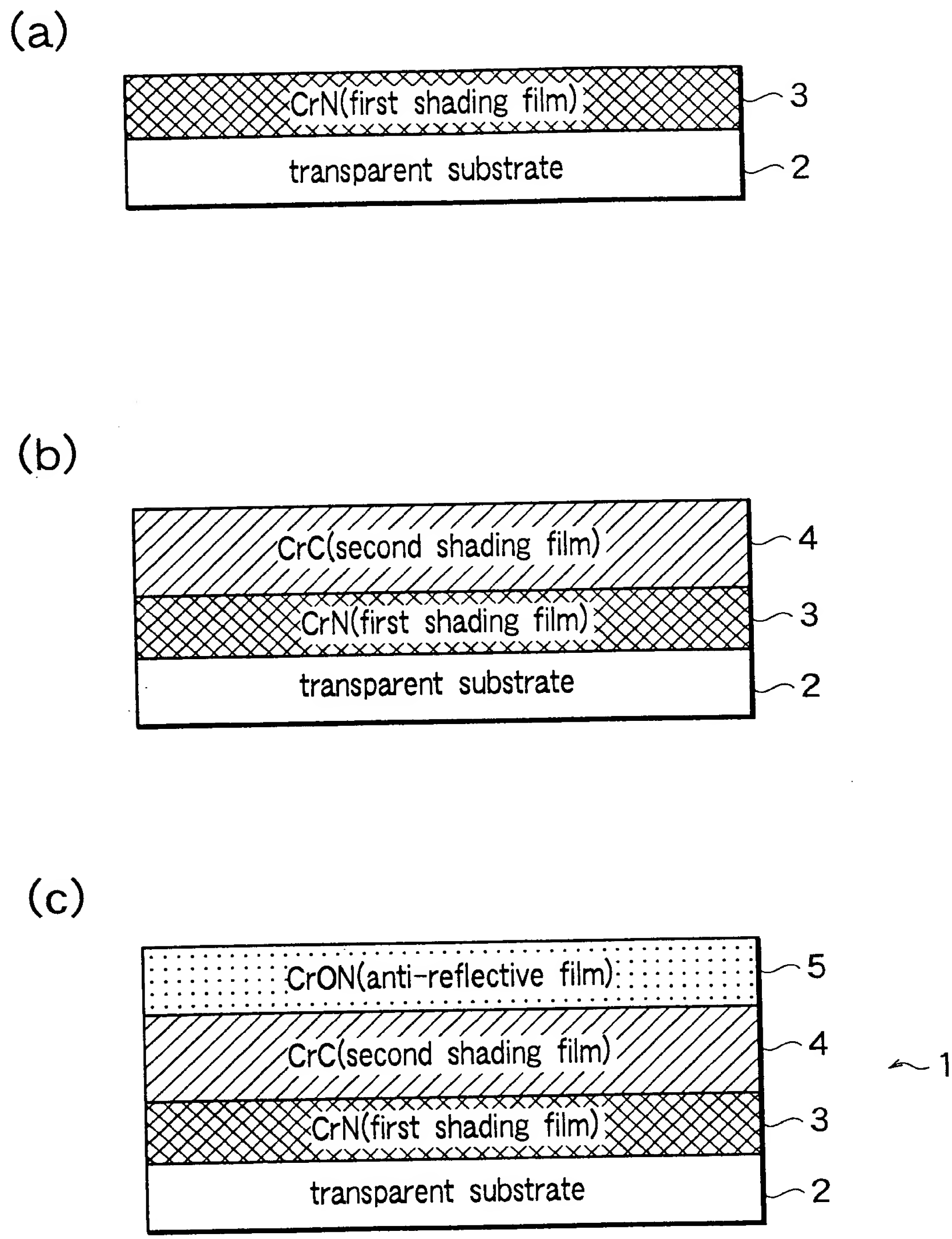
[DRAWINGS]
[FIG. 1]



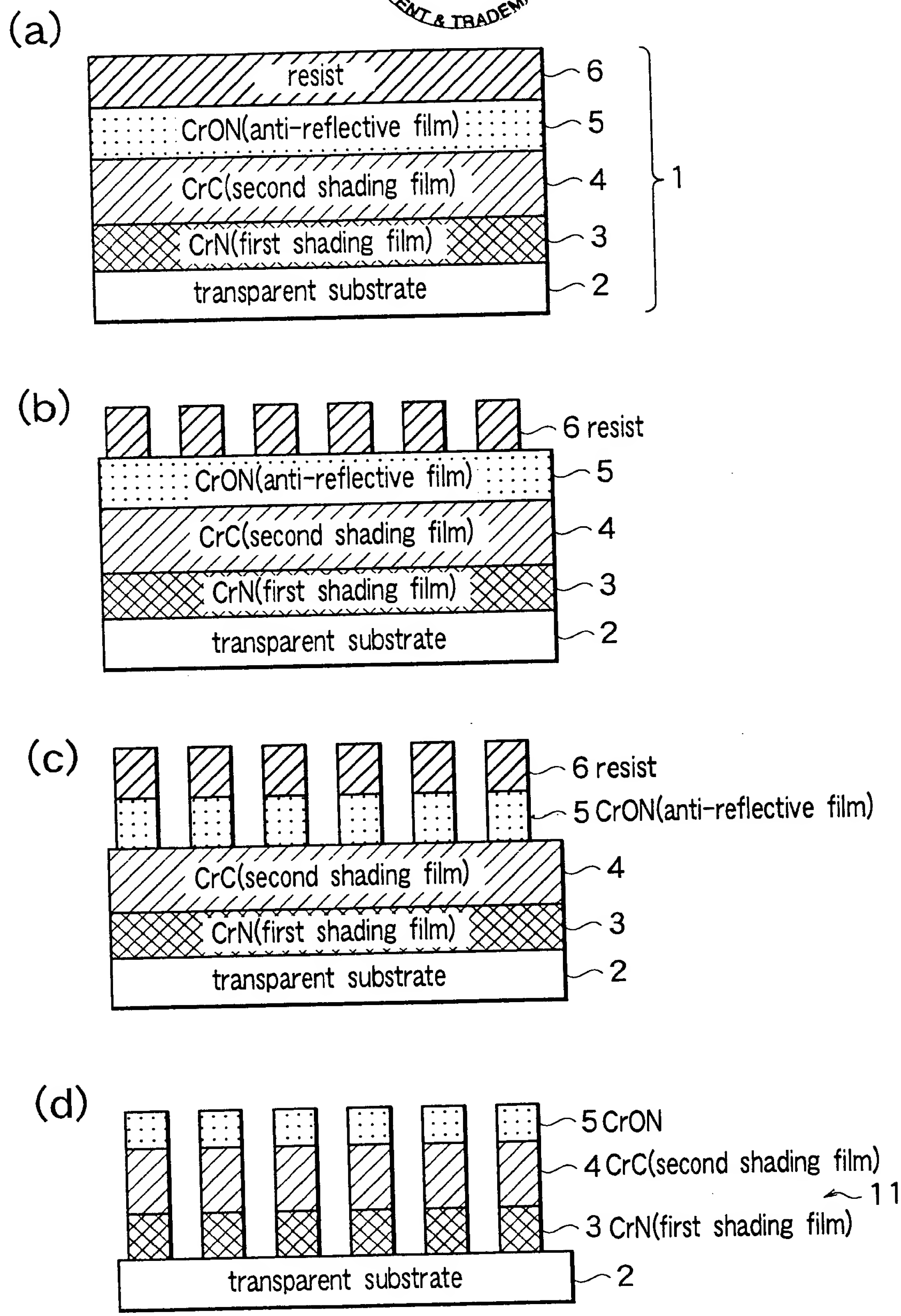
[FIG. 2]



[FIG. 3]

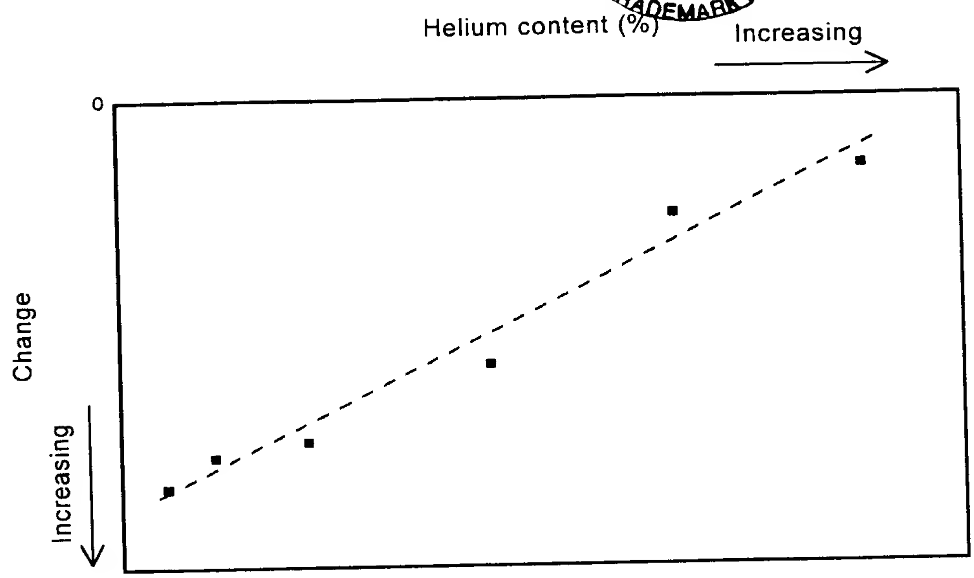

(a)
CrN(first shading film)
3
transparent substrate
2
(b)
CrC(second shading film)
4
CrN(first shading film)
3
transparent substrate
2
(c)
CrON(anti-reflective film)
5
CrC(second shading film)
4
1
CrN(first shading film)
3
transparent substrate
2

[FIG. 4]

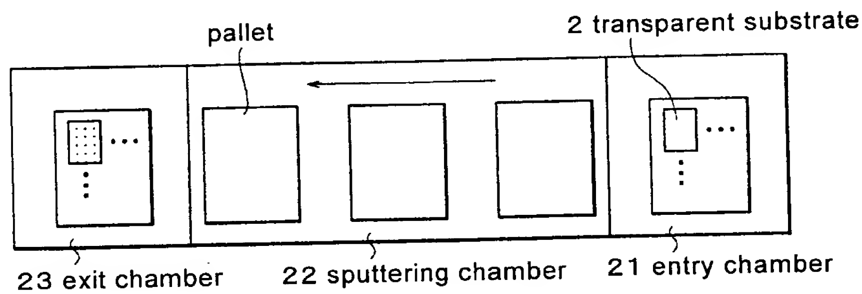


(a)
resist
6
CrON(anti-reflective film)
5
CrC(second shading film)
4
1
CrN(first shading film)
3
transparent substrate
2
(b)
6 resist
CrON(anti-reflective film)
5
CrC(second shading film)
4
CrN(first shading film)
3
transparent substrate
2
(c)
6 resist
5 CrON(anti-reflective film)
CrC(second shading film)
4
CrN(first shading film)
3
transparent substrate
2
(d)
5 CrON
4 CrC(second shading film)
11
3 CrN(first shading film)
transparent substrate
2

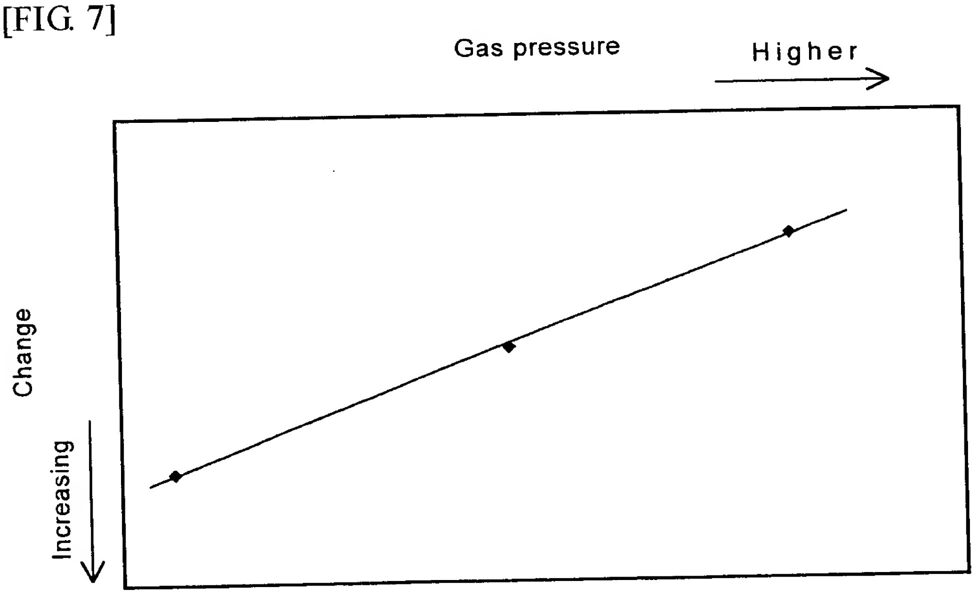
[FIG. 5]



[FIG. 6]



[FIG. 7]



[DOCUMENT NAME] ABSTRACT

[ABSTRACT]

[PROBLEM]

Obtaining a photomask blank having thin films with low film stress, good film quality, and which can be produced at a high yield in mass production.

[RESOLVING MEANS]

In obtaining a photomask blank 1 by disposing a sputtering target in a vacuum chamber and forming thin films 3, 4, and 5 with a three-layer construction of CrN/CrC/CrON over a transparent substrate 2 by reactive sputtering, the thin films are formed in a mixed gas atmosphere containing helium, and the helium gas flux in the mixed gas is controlled such that the crystal grain diameter of the CrC thin film, which is the thickest film, will be 3 to 7 nm.

[SELECTED DRAWING] FIG. 1